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(54) Title: COLOURANTS ENCAPSULATED IN A POLYMER MATRIX

(57) Abstract: Polymeric particles comprising a polymeric matrix and colourant distributed throughout the matrix, wherein the polymeric matrix that has been formed from a blend of monomers comprising a first monomer which is an ethylenically unsaturated ionic monomer and a second monomer which is an ethylenically unsaturated hydrophobic monomer which is capable of forming a homopolymer of glass transition temperature in excess of 50 °C, and in which the first monomer is a salt of a volatile counterion component, characterised in that the polymeric matrix is impermeable to the colourant. The particles obtainable by the process of the invention can be used in a variety of industrial processes, for instance in the manufacture of inks, paper and cosmetics.

WO 02/090445 A1

## COLOURANTS ENCAPSULATED IN A POLYMER MATRIX

The present invention concerns a process for making polymeric particles containing entrapped colourants.

Entrapment of active ingredients can be achieved by a number of processes. Some of these techniques involve forming a polymeric shell around a central core or active ingredient. Other methods involve preparing a matrix of polymeric material throughout which an active ingredient is distributed.

Various methods for making capsules have been proposed in the literature. For instance it is known to encapsulate hydrophobic liquids by dispersing the hydrophobic liquid into an aqueous medium containing a melamine formaldehyde pre-condensate and then reducing the pH resulting in an impervious aminoplast resin shell wall surrounding the hydrophobic liquid. Variations of this type of process are described in GB-A-2073132, AU-A-27028/88 and GB-A-1507739, in which the capsules are preferably used to provide encapsulated inks for use in pressure sensitive carbonless copy paper.

However, although capsules based on melamine formaldehyde resins are both impervious and durable, they tend to suffer the disadvantage that they are less impermeable at elevated temperatures. In addition there is also a risk that at elevated temperatures formaldehyde is evolved.

Typical techniques for forming a polymer shell are described in, for instance, GB 1,275,712, 1,475,229 and 1,507,739, DE 3,545,803 and US 3,591,090.

In US 3,838,007 droplets of enzyme dispersed in an aqueous solution of, for instance, gelatin are dispersed into water and then cross-linked, to give cross linked particles of the gelatin containing the enzyme.

In EP-A-356,240 processes for encapsulating enzyme or other biologically

produced material; in a matrix of polymeric material by mixing the polymeric material with aqueous liquor containing the biologically produced material, dispersing this mixture in a water immiscible liquid and azeotroping the dispersion. The product can either be relatively coarse beads that can be recovered or a stable dispersion of small particles in the water immiscible liquid.

In EP-A-356,239 there is a description of various compositions and processes primarily intended for the encapsulation of enzymes for liquid or other detergents. One type of product described therein comprises particles having a core comprising matrix polymer containing the enzyme, oil around the core and a polymer shell around the oil.

Particles of a matrix polymer containing an active ingredient can be formed as a dispersion in oil and this dispersion can then be dispersed in aqueous solution of an encapsulating polymer or blend of polymers and polymer deposition can then be caused to occur around the oil particles that contain the particles of matrix polymer that contain the active ingredient.

US 5,744,152 describes a process for forming polymer particles introduced as a solution of a water soluble salt with a volatile amine of a polymer that is relatively insoluble and non-swelling in acid throughout which the active ingredient is dispersed or dissolved, and which the solution is heated to form the dry matrix and to volatilise the amine and thereby form a polymer that is insoluble in acid. The release of an active ingredient can be controlled by careful adjustment of the pH. This method is specifically designed for the entrapment of relatively large sized ingredients, in particular enzymes, fungi, spores, bacteria, cells or antibiotics, which are released by pH adjustment as a suitable release mechanism.

WO 97/24178 describes a particulate composition comprises particles having a polymeric matrix including a detergency active ingredient, wherein the polymeric matrix is formed of a free base form of a cationic polymer which is a co-polymer of an ethylenically unsaturated hydrophobic monomer with an ethylenically

unsaturated substituted amine monomer. The matrix particles can be made by polymerising the free base monomer and the hydrophobic monomer while dissolved in an organic solvent so as to form a solution of the free base polymer inorganic solvent. This is followed by addition of an aqueous solution of a volatile acid wherein the solvent has higher volatility than the acid. The solvent is then distilled off so as to leave a solution in water of the salt form of the polymer. A suitable volatile acid is acetic acid, in which event a suitable solvent is *n*-butyl acetate. The active ingredients particularly include enzymes which can be released by dilution of the medium in which they are contained.

All of the aforementioned references are concerned with entrapment or encapsulation of active ingredients, which are to be released at a later stage and thus do not give any indication of how to achieve permanent entrapment of materials, particularly relatively small sized species

A variety of techniques are known for providing encapsulated or entrapped colourants.

WO 91/06277 describes cosmetic formulations which have activatable dormant pigments dispersed in an anhydrous base or vehicle. Ground pigment or liquid carrier dispersion is microencapsulated to form stable, dry, free flowing powder of micro-sized particles. The preferred process of encapsulation is by coacervation e.g. by emulsifying a liquid dispersion in a continuous, external aqueous phase to form micro-sized droplets and a complex of colloidal material is added to the external phase in such a way to form a deposit on or around each droplet thereby forming an outer wall or shell. The microcapsules are intended to rupture and release the dormant pigment when subjected to physical forces.

US5234711 concerns methods of encapsulating pigment particles useful in manufacturing of cosmetic products. It is an objective of this disclosure to employ a vinyl-polymeric encapsulation process for increasing the wettability, dispersibility and heat resistance of the pigment particles. The method encapsulation involves

redox or free radical vinyl polymerisation in an aqueous medium.

EP 225799 describes microencapsulated solid non-magnetic colourant material in a liquid, gel, waxy or low temperature melting solid carrier phase which is encapsulated within a polymeric shell. Absorbed onto the shell is a silane or titanate coupling agent which increases the oleophilicity of the surface of the solid colourant material.

EP 445342 relates to a cosmetic composition comprising a pigment that has been formed by incorporating a solvated dye into a resin and admixing with a cosmetic carrier. The amount of pigment present is sufficient to provide attractive amount of pigment present sufficient to provide an attractive cosmetic effect when applied to skin, nails or hair. Any cosmetically acceptable soluble dye can be used. Any resin may be used provided it can be pulverised to a fine powder. The solvated dye may be incorporated into the resin by adding to the plasticised or molten resin; or by dissolving the dye in a solution of unpolymerised resin and mutual solvent for the dye and the resin, then polymerising the resin, or by contacting the dye with the resin. The dye impregnated resin powders are said to be used in a variety of cosmetic compositions.

Nevertheless there is a need to provide products containing entrapped or encapsulated colourants, which products retain the colourant over longer periods and also when subjected to different environments. This is especially so in the case of oil soluble and particularly water soluble dyes, where it is generally difficult to permanently retain the dye. In a cosmetic composition if the dye is not permanently retained, this can impair the long term visual effect of the cosmetic.

An objective of the present invention is to provide polymer entrapped colourants in which the colourant does not leach out even after prolonged use. Specifically it would be desirable to provide a process for entrapping solutions of dyes in polymeric particles for incorporation into cosmetic formulations and wherein the dyes remain permanently entrapped and are not released before during or after

application.

In addition encapsulation or entrapment of colourants can result in visual impairment of the colourant. This may be as a result of the polymer absorbing light from certain wavelengths or sometimes as a result of the irregular morphology of the polymer particles.

In addition it is also an objective to provide an alternative method for converting oil soluble or water dyes into a product which can be used as a pigment in a variety of applications.

Thus a further objective of the present is to provide polymer entrapped colourants which yield improved visual effects

Thus according to the present invention we provide polymeric particles comprising a polymeric matrix and colourant distributed throughout the matrix, wherein the polymeric matrix that has been formed from a blend of monomers comprising a first monomer which is an ethylenically unsaturated ionic monomer and a second monomer which is an ethylenically unsaturated hydrophobic monomer which is capable of forming a homopolymer of glass transition temperature in excess of 50°C, and in which the first monomer is a salt of a volatile counterion component, characterised in that the polymeric matrix is impermeable to the colourant.

In a further aspect of the present invention we provide a process of preparing polymeric particles comprising a polymeric matrix and colourant distributed throughout the matrix, wherein the polymeric matrix that has been formed from a blend of monomers comprising a first monomer which is an ethylenically unsaturated ionic monomer and a second monomer which is an ethylenically unsaturated hydrophobic monomer which is capable of forming a homopolymer of glass transition temperature in excess of 50°C,

and in which the first monomer is a salt of a volatile counterion component, wherein the polymeric matrix is impermeable to the colourant, which process comprises the steps,

- A) providing an aqueous phase of a polymeric salt formed from a monomer blend which comprises the first and second
- B) dissolving or dispersing the colourant with the aqueous phase,
- C) forming a dispersion consisting essentially of the aqueous phase in a water immiscible liquid phase which comprises an amphipathic polymeric stabiliser to form an emulsion, and
- D) subjecting the dispersion to dehydration wherein water is evaporated from the aqueous particles thereby forming solid particles comprising the colourant distributed throughout the matrix polymer, wherein volatile counterion component of the salt is evaporated during the distillation and the matrix polymer is converted to its free acid or free base form.

The particles according to the first aspect of the invention and the products resulting from the process according to the second aspect of the invention have enhanced visual performance and furthermore the polymer matrix does not allow any of the entrapped colourant to be released even under prolonged use.

The polymeric products can be further enhanced if the polymeric matrix is cross-linked. This cross-linking can be as a result of including a cross-linking step in the process. This can be achieved by including self cross-linking groups in the polymer, for instance monomer repeating units carrying a methylol functionality. Preferably though the cross-linking is achieved by including a cross-linking agent with the aqueous phase polymer. The cross-linking agent are generally compounds which react with functional groups on the polymer chain. For instance when the polymer chain contains anionic groups a suitable cross-linking agent may be aziridine, diepoxides, carbodiimides, silanes or a multivalent metal, for instance aluminium or zirconium. One particularly preferred cross-linking agent is ammonium zirconium carbonate. Another particularly preferred class of cross-linking agent include compounds which form covalent bonds between polymer

chains, for instance silanes or diepoxides.

The cross-linking process desirably occurs during the dehydration step. Thus where a cross-linking agent is included, it will generally remain dormant until the dehydration is started.

We have found that polymers formed from the special combination of hydrophobic monomer that are capable of forming a homopolymer of glass transition temperature in excess of 50°C, preferably greater than 60 or 80°C exhibit considerably improved performance in regard to the impermeability to the colourant. By hydrophobic monomer we mean that the monomer has a solubility in water of less than 5g per 100 ml water.

Glass transition temperature ( $T_g$ ) for a polymer is defined in the Encyclopedia of Chemical Technology, Volume 19, fourth edition, page 891 as the temperature below which (1) the transitional motion of entire molecules and (2) the coiling and uncoiling of 40 to 50 carbon atom segments of chains are both frozen. Thus below its  $T_g$  a polymer would not exhibit flow or rubber elasticity. The  $T_g$  of a polymer may be determined using Differential Scanning Calorimetry (DSC). Thus a reference sample with known  $T_g$  and the experimental sample are heated separately but in parallel according to a linear temperature programme. The two heaters maintain the two samples at identical temperatures. The power supplied to the two heaters to achieve this is monitored and the difference between them plotted as a function of reference temperature which translates as a recording of the specific heat as a function of temperature. As the reference temperature is increased or decreased and the experimental sample approaches a transition the amount of heat required to maintain the temperature will be greater or lesser depending on whether the transition is endothermic or exothermic. A typical plot indicating the glass transition temperature is shown in Figure 1.

Generally the average particle size diameter of the particles is less than about 100 microns. Usually the average particle size diameter tends to be smaller, for



instance less than 70 or 80 microns, often less than 40 or 50 microns and typically the average particle diameter will be between 750 nanometers and 40 microns. Preferably the average particle size diameter is in the range 10 to 40 microns usually between 20 and 40 microns. Average particle size is determined by a Coulter particle size analyser according to standard procedures well documented in the literature.

Without being limited to theory it is believed that the particular combination of ionic monomer and said hydrophobic monomer provides polymers with the right degree of hydrophilicity and hardness that seems to be responsible for the improvements in impermeability to the colourant.

Specific examples of said hydrophobic monomers include styrene, methyl methacrylate, tertiary butyl methacrylate, phenyl methacrylate, cyclohexyl methacrylate and isobornyl methacrylate.

It has been found that it is not possible to replace the hydrophobic monomers with ethylenically unsaturated carboxylic acid esters that are not capable of forming a homopolymer that has a glass transition temperature of at least 50°C without adversely increasing the permeability of the polymer. Preferably still the Tg should be at least 60°C or even at least 80°C. For instance substituting the hydrophobic monomer of the present invention by other (meth)acrylic esters, for instance 2-ethyl hexyl acrylate would be unsuitable. Best results are generally obtained by use of monomers which are capable of forming polymers of very high Tg. Therefore less preferred products would be produced using ethyl acrylate or propyl acrylate as the hydrophobic monomer.

The ionic monomer may contain either anionic or cationic groups or alternatively may be potentially ionic, for instance in the form of an acid anhydride. Preferably the ionic monomer is an ethylenically unsaturated anionic or potentially anionic monomer. Suitable anionic monomers include (meth)acrylic acid, maleic acid, maleic anhydride, itaconic acid, itaconic acid anhydride, crotonic acid, (meth) allyl

sulphonic acid, vinyl sulphonic acid and 2-acrylamido-2-methyl propane sulphonic acid. Preferred anionic monomers are carboxylic acids or acid anhydrides.

When the ionic monomer is anionic, for instance a carboxylic acid or anhydride the volatile counterion may be ammonia or a volatile amine component. Thus the polymer may be produced in free acid form and then neutralised with an aqueous solution of ammonium hydroxide or a volatile amine, for instance ethanolamine. Alternatively the polymer may be prepared by copolymerising the ammonium or volatile amine salt of an anionic monomer with the hydrophobic monomer.

Generally the matrix polymer may be prepared by any suitable polymerisation process. For instance the polymer can be conveniently prepared by aqueous emulsion polymerisation for instance as described in EP-A-697423 or US-A-5070136. The polymer can then be neutralised by the addition of an aqueous solution of ammonium hydroxide or a volatile amine.

In a typical polymerisation process the blend of hydrophobic monomer and anionic monomer is emulsified into an aqueous phase which contains a suitable amount of emulsifying agent. Typically the emulsifying agent may be any commercially available emulsifying agents suitable for forming aqueous emulsion. Desirably these emulsifying agents will tend to be more soluble in the aqueous phase than in the monomer water immiscible phase and thus will tend to exhibit a high hydrophilic lipophilic balance (HLB). Emulsification of the monomer may be effected by known emulsification techniques, including subjecting the monomer/aqueous phase to vigorous stirring or shearing or alternatively passing the monomer/aqueous phase through a screen or mesh. Polymerisation may then be effected by use of suitable initiator systems, for instance UV initiator or thermal initiator. A suitable technique of initiating the polymerisation would be to elevate the temperature of the aqueous emulsion of monomer to above 70 or 80°C and then add between 50 and 1000 ppm ammonium persulphate by weight of monomer.

Generally the matrix polymer has a molecular weight of up to 200,000 (Determined by GPC using the industry standard parameters). Preferably the polymer has a molecular weight of below 50,000, for instance 2,000 to 20,000. Usually the optimum molecular weight for the matrix polymer is around 8,000 to 12,000.

Typically the monomer blend may contain at least 50% by weight hydrophobic monomer, the remainder being made up of anionic monomer. Generally though the hydrophobic monomer will be present in amounts of at least 60% by weight. Preferred compositions contain between 65 and 90% by weight hydrophobic polymer, for instance around 70 or 75%.

A particularly preferred matrix polymer is a copolymer of styrene with ammonium acrylate. More preferably this polymer is used when the process employs a cross-linking agent, which is especially ammonium zirconium carbonate.

In an alternative version of the process of the present invention the ionic monomer may be cationic or potentially cationic, for instance an ethylenically unsaturated amine. In this form of the invention the volatile counterionic component is a volatile acid component. Thus in this form of the invention the matrix polymer can be formed in an analogous way to the aforementioned anionic matrix polymer, except that the anionic monomer is replaced by a cationic or potentially cationic monomer. Generally where the polymer is prepared in the form of a copolymer of a free amine and hydrophobic monomer, it is neutralised by including a suitable volatile acid, for instance acetic acid, formic acid or even carbonic acid. Preferably the polymer is neutralised by a volatile carboxylic acid.

The amount of cationic or potentially cationic monomer to hydrophobic monomer is generally the same as for the aforementioned anionic monomer.

The particles may entrap one or more colourants and the colourant may be any colourant, for instance a dye, pigment or lake. Typically suitable colourants include

any organic or inorganic pigment or colourant approved for use in cosmetics by CTFA and the FDA such as lakes, iron oxides, titanium dioxide, iron sulphides or other conventional pigments used in cosmetic formulations. Examples of the pigment include an inorganic pigment such as carbon black, D&C Red 7, calcium lake, D&C Red 30, talc Lake, D&C Red 6, barium lake, Russet iron oxide, yellow iron oxide, brown iron oxide, talc, kaolin, mica, mica titanium, red iron oxide, magnesium silicate and titanium oxide; and organic pigment such as Red No 202, Red No 204, Red No 205, Red No 206, Red No 219, Red No 228, Red No 404, Yellow No 205, Yellow No 401, Orange No 401 and Blue No 404. Examples of oil soluble dyes include Red No 505, Red No 501, Red No 225, Yellow No 404, Yellow No 405, Yellow No 204, Orange No 403, Blue No 403, Green No 202 and Purple No 201. Examples of vat dyes are Red No 226, Blue No 204 and Blue No 201. Examples of lake dye include various acid dyes which are laked with aluminium, calcium or barium.

Conventional dyes may also be used and may be either oil or water soluble. Preferably the colourant is an aqueous solution of a water soluble dye. Suitable dyes for the present invention include FD & C Blue No 11, FD & C Blue No 12, FD & C Green No 13, FD & C Red No 13, FD & C Red No 140, FD&C Yellow No. 15, FD&C Yellow No. 16, D&C Blue No. 14, D&C Blue No. 19, D&C Green No. 15, D&C Green No. 16, D&C Green No. 18, D&C Orange No. 14, D&C Orange No. 15, D&C Orange No. 110, D&C Orange No. 111, D&C Orange No. 117, FD&C Red No. 14, D&C Red No. 16, D&C Red No. 17, D&C Red No. 18, D&C Red No. 19, D&C Red No. 117, D&C Red No. 119, D&C Red No. 121, D&C Red No. 122, D&C Red No. 127, D&C Red No. 128, D&C Red No. 130, D&C Red No. 131, D&C Red No. 134, D&C Red No. 139, FD&C Red No. 140, D&C Violet No. 12, D&C Yellow No. 17, Ext. D&C Yellow No. 17, D&C Yellow No. 18, D&C Yellow No. 111, D&C Brown No. 11, Ext. D&C Violet No. 12, D&C Blue No. 16 and D&C Yellow No. 110. Such dyes are well known, commercially available materials, with their chemical structure being described, e.g., in 21 C.F.R. Part 74 (as revised April 1, 1988) and the CTFA Cosmetic Ingredient Handbook, (1988), published by the Cosmetics, Toiletry and Fragrancy Association, Inc. These publications are

incorporated herein by reference.

The colourant can be a substance which is a dormant colourant, for instance a colour former which exhibits a colour on exposure to a suitable trigger mechanism, for instance heat or irradiation. Suitably such entrapped colour formers can be coated onto or incorporated into a suitable substrates and then treated to exhibit the colour. The advantage of providing colour formers as polymeric particles is that they can be more easily be processed and incorporated into the substrate in a desired way. The colour former can still be activated even though it is entrapped within the polymer particle.

The colourant may also be a fluorescent compound and/or a chromophor compound. Suitably the colourant can be fluorescent whitening agent (FWA).

The process of the present invention involves dispersing the aqueous solution of matrix polymer containing colourant into a water immiscible liquid. Typically the water immiscible liquid is an organic liquid or blend of organic liquids. The preferred organic liquid is a mixture of a non-volatile paraffin oil and a volatile paraffin oil. The two oils may be used in equal proportions by weight, but generally it is often preferred to use the non-volatile oil in excess, for instance greater than 50 to 75 parts by weight of the non-volatile oil to 25 to less than 50 parts by weight of the volatile oil.

In the process according to the second aspect of the invention it is desirable to the present invention to include a polymeric amphipathic stabiliser in the water immiscible liquid. The amphipathic stabiliser may be any suitable commercially available amphipathic stabiliser, for instance HYPERMER (RTM) (available from ICI). Suitable stabilisers also include the stabilisers described in WO-A-97/24179. Although it is possible to include other stabilising materials in addition to the amphipathic stabiliser, such as surfactants, it is generally preferred that the sole stabilising material is the amphipathic stabiliser.

In the process of the present invention the dehydration step can be achieved by

any convenient means. Desirably dehydration can be effected by subjecting the dispersion in oil to vacuum distillation. Generally this will require elevated temperatures, for instance temperatures of 30°C or higher. Although it may be possible to use much higher temperatures e.g. 80 to 90°C it is generally preferred to use temperatures of below 60 or 70°C.

Instead of vacuum distillation it may be desirable to effect dehydration by spray drying. Suitably this can be achieved by the spray drying process described in WO-A-97/34945.

The dehydration step removes water from the aqueous solution of matrix polymer and also the volatile counterion component, resulting in a dry polymer matrix which is insoluble and non-swelling in water, containing therein the colourant which is distributed throughout the polymeric matrix.

The invention also includes the polymeric particles which are obtainable by the process of the second aspect of the present invention.

In a further aspect of the present invention we provide a cosmetic composition comprising a cosmetically acceptable base and polymeric particles in accordance with the first aspect of the invention or products obtained according to the process of the second aspect of the invention.

The following examples illustrate the invention.

**Example 1. - Preparation of Blue Dye Polymer Particles in Oil.**

An aqueous solution is formed by dissolving 10g of Cibracron Blue P2R dye in 396g of 25% solution of a copolymer of styrene and ammonium acrylate and then addition of 9.9g of 50% ammonium zirconium carbonate.

An oil solution is prepared by mixing 50g of 20% polymeric stabiliser, 89g of Kristol M14 oil and 70.4g of Isopar G solvent.

The aqueous solution is added to the agitated oil solution and then homogenised with a high shear Silverson mixer to form a water-in-oil emulsion. After 15 minutes of emulsification, extra 179g of Isopar G is added as a diluent.

The resulting emulsion is transferred to a resin pot having vacuum distillation capabilities. The emulsion is warmed to 25°C and water/Isopar G mixture distilled under reduced pressure at a constant temperature of about 30°C. The volume of water and solvent is monitored and distillation continued until no further water is collected in the distillate and then temperature is allowed to rise to 100°C under vacuum. The dried dye polymer particles in oil are then held at 100°C for 60 minutes to drive off ammonia and crosslink the carboxylated styrene based matrix polymer to the water insoluble form.

The contents of flask are cooled. The dispersion of Dye polymer particles in oil is stable and having an average of diameter of less than 2 microns.

**Example 2. - Preparation of Red Dye Polymer Particles in Oil.**

Example 1 was repeated with the exception that 10g of a water soluble red was used in place of the Cibracron Blue dye.

A red dye polymer particle dispersion in oil was obtained.

**Example 3. - Preparation of Red Pigment Polymer Particles in Oil.**

Example 1 was repeated with the exception that 10g of a red pigment was dispersed in the aqueous solution of the polymer solution.

A dispersion in oil of red pigment encapsulated in a polymer matrix was obtained.

Example 4 - Dehydration Using Spray Drying

Example 1 was repeated except instead of dehydrating using vacuum distillation, the spray drying process described by Example 1 of WO-A-97/34945 was used.



**Claims**

1. Polymeric particles comprising a polymeric matrix and colourant distributed throughout the matrix, wherein the polymeric matrix that has been formed from a blend of monomers comprising a first monomer which is an ethylenically unsaturated ionic monomer and a second monomer which is an ethylenically unsaturated hydrophobic monomer which is capable of forming a homopolymer of glass transition temperature in excess of 50°C, and in which the first monomer is a salt of a volatile counterion component, characterised in that the polymeric matrix is impermeable to the colourant.
2. Polymeric particles according to claim 1 in which the polymeric matrix comprises polymer which is in free acid or free base form.
3. Polymeric particles according to claim 1 or claim 2 in which the polymeric matrix is cross-linked.
4. Polymeric particles according to any of claims 1 to 3 in which the polymeric particles have an average particle size of below 100 microns, preferably below 50 microns.
5. Polymeric particles according to any of claims 1 to 4 in which the second monomer is selected from the group consisting of styrene, methyl methacrylate, acrylonitrile, tertiary butyl methacrylate, phenyl methacrylate, cyclohexyl methacrylate and isobornyl methacrylate.
6. Polymeric particles according to any of claims 1 to 5 in which the first monomer is an ethylenically unsaturated carboxylic acid and the volatile counterion component is ammonia or a volatile amine.
7. Polymeric particles according to any of claims 1 to 6 in which the matrix polymer is a copolymer of styrene with ammonium acrylate and ammonium zirconium carbonate is used as a cross-linking agent.
8. Polymeric particles according to any of claims 1 to 7 in which the colourant is a dye, pigment or lake.
9. A process of preparing polymeric particles comprising a polymeric matrix and colourant distributed throughout the matrix, wherein the polymeric matrix that has been formed from a blend of monomers comprising a first monomer which is an ethylenically unsaturated ionic monomer

and a second monomer which is an ethylenically unsaturated hydrophobic monomer which is capable of forming a homopolymer of glass transition temperature in excess of 50°C,

and in which the first monomer is a salt of a volatile counterion component, wherein the polymeric matrix is impermeable to the colourant, which process comprises the steps,

B) providing an aqueous phase of a polymeric salt formed from a monomer blend which comprises the first and second

B) dissolving or dispersing the colourant with the aqueous phase,

C) forming a dispersion consisting essentially of the aqueous phase in a water immiscible liquid phase which preferably comprises an amphipathic polymeric stabiliser to form an emulsion, and

D) subjecting the dispersion to dehydration wherein water is evaporated from the aqueous particles thereby forming solid particles comprising the colourant distributed throughout the matrix polymer,

wherein volatile counterion component of the salt is evaporated during the distillation and the matrix polymer is converted to its free acid or free base form.

10. A process according to claim 9 in which a cross-linking agent is included in the aqueous phase and the matrix polymer becomes cross-linked during the dehydration step.

11. A process according to claim 9 or 10 in which the polymeric particles have an average particle size of below 100 microns, preferably below 50 microns.

12. A process according to any of claims 9 to 11 in which the second monomer is selected from the group consisting of styrene, methyl methacrylate, acrylonitrile, tertiary butyl methacrylate, phenyl methacrylate, cyclohexyl methacrylate and isobornyl methacrylate.

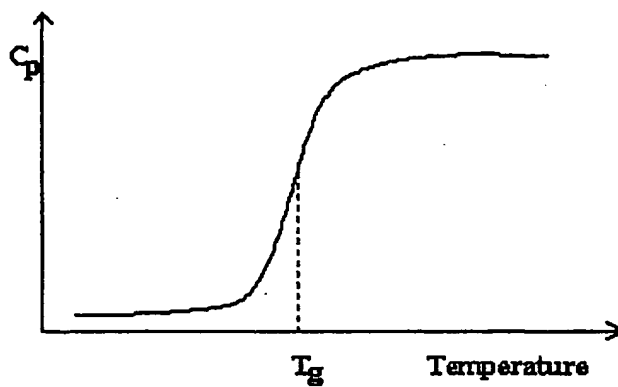
13. A process according to any one of claims 9 to 12 in which the first monomer is an ethylenically unsaturated carboxylic acid and the volatile counterion component is ammonia or a volatile amine.

14. A process according to any one of claims 9 to 13 in which the polymeric matrix is a copolymer of styrene with ammonium acrylate and ammonium zirconium carbonate is used as a cross-linking agent.

15. A process according to any one of claims 9 to 14 in which the first monomer is an ethylenically unsaturated amine and the volatile counterion component is a volatile carboxylic acid.
16. A process according to any one of claims 9 to 15 in which the colourant is a dye, pigment or lake, preferably an aqueous solution of a water soluble dye.
17. A process according to any one of claims 9 to 16 in which the dehydration step involves vacuum distillation.
18. A process according to any one of claims 9 to 17 in which the dehydration step involves spray drying.
19. A cosmetic composition comprising a cosmetically acceptable base and polymeric particles as defined by any of claims 1 to 8 or prepared by the process according to any of claims 9 to 18.

Figure 1

1/1



# INTERNATIONAL SEARCH REPORT

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C09B67/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, CHEM ABS Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 744 152 A (SYMES KENNETH CHARLES ET AL) 28 April 1998 (1998-04-28) cited in the application the whole document	1-19
A	US 3 876 603 A (MAKHLOUF JOSEPH M) 8 April 1975 (1975-04-08) the whole document	1-19
A	WO 97 24178 A (ALLIED COLLOIDS LTD ; LANGLEY JOHN GRAHAM (GB); MISTRY KISHOR KUMAR) 10 July 1997 (1997-07-10) cited in the application the whole document	1-19
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
<b>* Special categories of cited documents:</b>		
*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *d* document member of the same patent family		
Date of the actual completion of the international search  1 October 2002		Date of mailing of the international search report  09/10/2002
Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2260 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer  Fritz, M

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## Continuation of Box I.2

Present claims 1-6,8-13,15-19 relate to a products and processes defined by reference to a desirable characteristic or property, namely a combination of two monomers which is capable of forming a homopolymer of glass transition temperature in excess of 50 degrees Celsius.

The claims cover all products and processes having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products and processes. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the products and processes by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely

those products and processes in which

- the first monomer is as defined on p. 8, 3rd paragraph
- the second monomer is as defined on p. 8, last three lines - p. 9, first two lines
- the volatile counterion is
  - a. (if the ionic monomer is anionic) ammonia (cf. examples) or ethanolamine (p. 9, second paragraph)
  - b. (if the ionic monomer is cationic) acetic acid, formic acid or carbonic acid (p. 10, 4th paragraph)

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 02/04348

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 02/04348

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5744152	A	28-04-1998	AU 637323 B2 27-05-1993
			AU 4022289 A 08-03-1990
			AU 637577 B2 03-06-1993
			AU 4022689 A 01-03-1990
			AU 634719 B2 04-03-1993
			AU 4022789 A 01-03-1990
			CA 1336694 A1 15-08-1995
			CA 1339108 A1 29-07-1997
			DE 68910925 D1 05-01-1994
			DE 68910925 T4 23-02-1995
			DE 68919942 D1 26-01-1995
			DE 68919942 T2 27-07-1995
			DE 68921266 D1 30-03-1995
			DE 68921266 T2 22-06-1995
			DK 2796 A 12-01-1996
			DK 171065 B1 13-05-1996
			DK 171073 B1 28-05-1996
			DK 171054 B1 06-05-1996
			EP 0361677 A1 04-04-1990
			EP 0356239 A2 28-02-1990
			EP 0356240 A2 28-02-1990
			EP 0626445 A2 30-11-1994
			FI 893957 A ,B, 25-02-1990
			FI 893958 A 25-02-1990
			FI 893959 A ,B, 25-02-1990
			GR 3015411 T3 30-06-1995
			JP 2102298 A 13-04-1990
			JP 2639844 B2 13-08-1997
			JP 2111718 A 24-04-1990
			JP 2824786 B2 18-11-1998
			JP 2150280 A 08-06-1990
			JP 2992558 B2 20-12-1999
			NO 893388 A ,B, 26-02-1990
			NO 893389 A ,B, 26-02-1990
			NO 893390 A ,B, 26-02-1990
			US 5460817 A 24-10-1995
			US 5035900 A 30-07-1991
			US 5324445 A 28-06-1994
			US 5492646 A 20-02-1996
US 3876603	A	08-04-1975	NONE
WO 9724178	A	10-07-1997	AU 1203797 A 28-07-1997
			WO 9724178 A1 10-07-1997
			ZA 9610929 A 30-12-1997